

Potentiality of Steric and Compression Effect in Conformational Analysis : A ^{13}C NMR Study

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Conformational analysis by ^{13}C NMR spectroscopy about $\text{N}_{\text{sp}^2} - \text{C}_{\text{sp}^2}$ bond in *endo/exo* isomeric systems of bicyclo-5-heptene-2,3-N-aryl dicarboximides have demonstrated that the steric and compression effect of the non-planar cage is quite diagnostic in the study of rotational processes. In cases of *exo*-N-aryl imides where, ^1H NMR is not very sensitive, ^{13}C NMR provides conclusive evidence about the rotational mode of the phenyl ring about the N-C bond.

Key Words: *endo/exo*, *syn/anti*, Conformational analysis, Asymmetric cage, ^{13}C NMR.

INTRODUCTION

Restricted rotation and two non-planar conformations about N-C bond in *o*-substituted aryl imides have been demonstrated through ^1H NMR spectroscopy employing asymmetric cage moieties. The existence of two non-planar *syn/anti* conformations has been explained with the help of shielding parameters and chemical shifts on the NMR time scale^{1,2}. The restricted rotation about N-N bond and isomeric separation of hydrazones due to lone pair of nitrogen has been reported³.

The stereoelectronic control on the torsional energy barrier due to rotation about (N-C) phenyl bond helps in the separation of atropisomers and has been studied by ^1H NMR spectroscopy^{4,5}. ^{13}C NMR spectroscopic technique has been applied to study the rotational process about $\text{N}_{\text{sp}^2} - \text{C}_{\text{sp}^2}$ bond in system (1) and found to be advantageous over the ^1H NMR spectroscopy particularly, when the *ortho*-substituent does not contain a proton⁶. Conformational study about N-C (phenyl) bond employing *endo/exo* isomeric systems of bicyclo-5-heptene-2,3-dicarboximides by ^1H NMR spectroscopy has shown duplexed signals for the *o*-substituent in the *endo* configuration (2) whereas, in the *exo*-system (3) no such evidence has been shown for the two conformations. Though, the anisotropic effect in ^{13}C NMR is of lower magnitude as compared to ^1H NMR spectroscopy, the potentiality of compression effect has been shown in stereochemical context⁷⁻¹³. To explore the potentiality ^{13}C NMR spectroscopy in such cases, spectral pattern of some isomeric (*endo/exo*) products has been described in this communication.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded on a FT-NMR Jeol FX-90Q spectrometer at 25° in CDCl_3 with tetramethylsilane as internal standard. VT NMR spectral measurements were made in $\text{DMSO}-d_6$ (Jeol NM-PVT Temperature controller, sensitivity $\pm 0.5^\circ\text{C}$).

Preparation of compounds: The compounds were obtained from cyclopentadiene and maleic anhydride *endo* and *exo* adducts and substituted aromatic amines as reported earlier⁷⁻¹³.

RESULTS AND DISCUSSION

^{13}C NMR spectrum of compound **I** suggests a fast rotation of the phenyl ring across the $\text{N}_{\text{sp}^2}\text{-C}_{\text{sp}^2}$ bond (Table-1). Compound **II** with a methyl group at the 2'-position exhibits the following ^{13}C NMR resonances: δ 17.66 and δ 18.91 for 2'- CH_3 carbon ($\Delta\delta = 1.25$ ppm), δ 45.18 and δ 45.51 for (2+3) carbons, δ 45.83 and δ 46.81 for (1+4) carbons, δ 52.33 and δ 52.77 for 7-carbons, δ 126.77 and δ 126.85 for 2'-carbon, δ 131.16 and δ 135.33 for (5+6) carbons along with aromatic carbon resonances at δ 128.29, 129.37 and 131.05 ppm.

The multiplicity in the signals for 2'- CH_3 carbon, (2+3) methine carbons, (5+6) olefinic carbons and for 2'-substituted carbon suggests the presence of two non-planar ground state conformations of the phenyl ring about the $\text{N}_{\text{sp}^2}\text{-C}_{\text{sp}^2}$ bond. The shielded methyl resonance (δ 17.66) corresponds to the *syn* orientation where, it experiences both the anisotropic effect and the steric compression effect of the cage olefinic system. The other methyl resonance (δ 18.91), corresponds to the *anti* conformation. The duplexed methyl resonances are temperature dependent which coalesce at 150° . ($\text{DMSO}-d_6$) and an energy barrier¹⁴⁻¹⁶ $\Delta G^\ddagger = 21.17$ kcal/mol has been evaluated for the involved rate process. Compounds **IV** and **VI** having -Cl and - OCH_3 groups at the 2'-position exhibit duplexity for the 2', 5+6 and 2+3 carbon resonances and suggest the slow rotation of the phenyl ring about N-C bond. The shielded resonances correspond to the *syn* conformation of the substituent in the phenyl ring.

In compounds **VIII-XIV**, the N-phenyl ring is arranged to experience the effect of methylene bridge. ^{13}C NMR spectrum of the compound **IX** exhibits the following characteristic resonances: δ 17.13 and δ 17.78 for the 2'- CH_3 carbon ($\Delta\delta = 0.65$ ppm), δ 44.43 and δ 45.08 for (2+3) carbons, δ 47.41 and δ 48.06 for 7- CH_2 carbon, δ 126.61 and δ 126.86 for 2'-carbon along with resonances at δ 46.65, 128.51, 129.05, 130.68, 131.87, 136.66, 137.77 ppm.

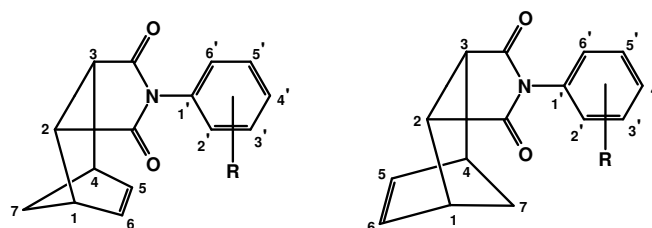
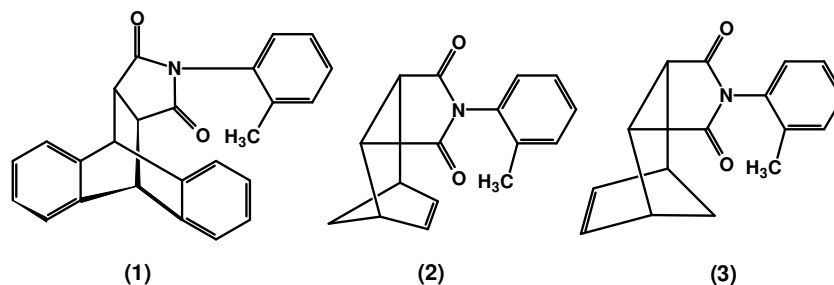
The duplexity exhibited by 2'- CH_3 carbon, (2+3) cage methine carbons, 7- CH_2 carbon is an evidence of the slow rotation and the presence of two non-planar conformations of the phenyl ring across the N-C bond. The methyl

TABLE-1
¹³C NMR SPECTRAL DATA OF COMPOUNDS I-VII

| Compd. | C=O | Substituents | C ₅ , C ₆ | C ₂ , C ₃ | Substituted carbon | C ₁ | Cage + aromatic carbons |
|------------|--------|--------------|---------------------------------|---------------------------------|--------------------|----------------|---|
| I | 176.67 | – | 135.39 | 45.41 | – | 134.52 | 46.01, 51.32, 126.29, 126.62, 128.40, 128.94 |
| II | 176.81 | 17.66, 18.91 | 131.16, 135.33 | 45.18, 45.51 | 126.77, 126.85 | 134.62 | 45.83, 46.81, 52.33, 52.77, 128.29, 129.37, 131.05 |
| III | 176.88 | 21.18 | 138.52 | 45.45 | 126.44 | 134.57 | 45.72, 52.17, 129.26, 129.64 |
| IV | 175.90 | – | 132.35, 135.06 | 45.34, 45.99 | 127.58, 129.69 | 134.62 | 46.86, 52.33, 130.13, 130.24, 130.39, 131.51 |
| V | 176.45 | – | 134.62 | 45.56 | 127.85 | 134.62 | 45.83, 52.28, 129.26 |
| VI | 176.66 | 55.53, 55.75 | 130.56, 134.57 | 45.29, 45.99 | 154.25 | 134.41 | 46.48, 51.95, 52.28, 112.14, 120.70, 128.29, 129.37 |
| VII | 177.04 | 55.42 | 134.52 | 45.40 | 159.44 | 134.52 | 45.67, 52.12, 114.36, 124.55, 127.80 |

TABLE-2
¹³C NMR SPECTRAL DATA OF COMPOUNDS VIII-XIV

| Compd. | C=O | Substituents | C ₇ | C ₂ , C ₃ | Substituted carbon | C ₁ | Cage + aromatic carbons |
|-------------|--------|--------------|----------------|---------------------------------|--------------------|----------------|---|
| VIII | 176.91 | – | 50.32 | 45.81 | – | 134.81 | 46.15, 126.56, 126.91, 128.82, 138.21 |
| IX | 176.67 | 17.13, 17.78 | 47.41, 48.06 | 44.43, 45.08 | 126.61, 127.86 | 135.17 | 46.65, 128.51, 129.05, 130.68, 131.87, 136.66, 137.77 |
| X | 176.56 | 21.92 | 51.56 | 45.96 | 127.99 | 135.62 | 46.86, 128.05, 129.66, 130.78, 137.87 |
| XI | 176.23 | – | 48.05, 48.43 | 43.07, 43.29 | 127.74, 129.31 | 134.81 | 45.67, 45.51, 130.02, 130.45, 130.56, 137.98 |
| XII | 177.98 | – | 5.06 | 45.12 | 129.68 | 134.99 | 45.84, 129.92, 130.18, 130.69, 138.24 |
| XIII | 177.11 | 55.75, 55.82 | 48.17, 48.32 | 45.25, 45.63 | 154.23, 154.41 | 134.82 | 45.84, 113.92, 121.32, 124.39, 128.72, 130.23, 137.14 |
| XIV | 176.26 | 55.91 | 51.06 | 45.43 | 156.43 | 134.86 | 45.81, 114.76, 122.03, 129.10, 130.16, 137.95 |



| | | | |
|------------|-------------------------|-------------|-------------------------|
| I | R = H | VIII | R = H |
| II | R = 2'-CH ₃ | IX | R = 2'-CH ₃ |
| III | R = 4'-CH ₃ | X | R = 4'-CH ₃ |
| IV | R = 2'-Cl | XI | R = 2'-Cl |
| V | R = 4'-Cl | XII | R = 4'-Cl |
| VI | R = 2'-OCH ₃ | XIII | R = 2'-OCH ₃ |
| VII | R = 4'-OCH ₃ | XIV | R = 4'-OCH ₃ |

resonances show temperature dependence and on raising the temperature coalesce at 145° (DMSO-*d*₆). Activation energy of the process has been evaluated to be $\Delta G_{\ddagger} = 22.0$ kcal/mol. Compounds **XI** and **XIII** also show duplexed signals for 7-endomethylene carbon and for 2'-carbon in ¹³C NMR spectrum (Table-2). The duplexity in resonances is attributed to compression effect and suggests two non-planar conformations of the phenyl ring due to slow rotation about N-C bond. In case of *exo* configuration (**IX**, **XI**, **XIII**), ¹H NMR spectroscopy could not provide evidence for the presence of different conformations while ¹³C NMR of these compounds demonstrated the two conformations about N-C bond. The increased value of activation energy in case of compound **IX** as compared to compound **II** suggests the role or compression effect of the non-planar cage moiety in controlling the rotation of phenyl of ring about N-C bond.

¹³C NMR spectra of 4'-substituted arylimides (**III**, **V**, **VII**, **X**, **XII** and **XIV**) exhibit normal spectral pattern and suggest a fast rotation of the phenyl ring about N-C bond as observed in unsubstituted arylimides.

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